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Maierson

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[54] **REPLACEMENT OF CAPSULE CONTENTS**

[75] Inventor: **Theodore Maierson,** Dayton, Ohio

[73] Assignee: **The National Cash Register Company,** Dayton, Ohio

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[58] **Field of Search** ..... 117/37 R, 36.2, 36.8, 117/36.9, 63

[56] **References Cited**

UNITED STATES PATENTS

R24,899	11/1960	Green	117/37 X
2,712,507	7/1955	Green	117/36.2 X
2,730,457	1/1956	Green et al.	117/36.2 X
2,800,457	7/1957	Green et al.	117/36.2 X
2,800,458	7/1957	Green	117/36.2 X
3,226,252	12/1965	Hemstock	117/36.2 X
3,317,433	5/1967	Eichel	117/36.8 X
3,432,327	3/1969	Kan et al.	117/36.9 X
3,516,943	6/1970	Brynko	117/36.2 X
3,540,914	11/1970	Lin	117/36.2 X
3,617,325	11/1971	Spokes et al.	117/36.2 X
3,653,945	4/1972	Davis et al.	117/36.8

Primary Examiner—William D. Martin
Assistant Examiner—Dennis C. Konopacki
Attorney—E. Frank McKinney et al.

[57] **ABSTRACT**

A process for replacing the contents of capsules without rupturing the capsule walls is disclosed. The capsules are subjected to water-miscible solvents and the capsule contents are replaced by diffusion. In the event color producing reactants are present, a color reaction is produced without rupturing the capsule walls. A preferred method of applying the water-miscible solvent is by employing a felt-tip marker.

2 Claims, No Drawings

REPLACEMENT OF CAPSULE CONTENTS

This invention relates to a process for replacing the contents of capsules. In another aspect, this invention relates to a method of marking. In still another aspect, this invention relates to a mark-forming unit.

Few processes for replacing the water-immiscible liquid contents of gelatin-walled capsules without rupturing the capsule walls are known in the art. One such process is described in U.S. Pat. No. 3,516,943. In this process, the capsules generally are immersed in a liquid exchange vehicle and the capsule walls preferably are in a swollen condition.

Other processes for replacing the water-immiscible liquid contents of gelatin-walled capsules generally require the application of pressure until a breach or rupture in the capsule wall occurs. One such process is described in U.S. Pat. No. 3,672,935, issued June 27, 1972.

A process now has been found for replacing the water-immiscible liquid contents of gelatin-walled capsules without rupturing the capsule walls. Gelatin capsules are subjected to water-miscible solvents. The solvent passes through the gelatin wall and mixes with the capsule contents. Once the initial penetration occurs, a release of water-miscible solvent-water-immiscible capsule content mixture occurs without rupture of the capsule wall. In the event color producing reactants are present in the water-miscible solvent, in the capsule or on the surface of the substrate, a color reaction is produced without rupturing the capsule wall. A preferred method for applying the water-miscible solvent is by employing a felt-tip marker.

Accordingly, an object of this invention is to provide a process for replacing the water-immiscible liquid contents of gelatin-walled capsules without rupturing the capsule walls.

Another object of this invention is to provide a method of marking without rupturing capsule walls.

Still another object of this invention is to provide a mark-forming unit comprising a felt-tip marker containing a water-miscible solvent and a coated substrate.

Other objects, aspects and advantages of this invention will be apparent to one skilled in the art from the following disclosure and appended claims.

In a preferred practice of this invention, an ink is encapsulated in microscopic capsules, which then are coated on base sheet record material. The ink comprises a liquid oil of a viscosity to act as an ink vehicle and colorless dye materials dissolved therein in the amount of several percent, as desired. The processes for the manufacture, en masse, in an aqueous manufacturing vehicle, of microscopic oil containing capsules having walls of film-forming hydrophilic polymeric material are known in the art, as are pressure-sensitive record materials. For examples, see U.S. Pat. Nos. 2,712,507; 2,730,457; 2,800,457; 2,800,458 and Rei. Pat. No. 24,899.

The solvents employed in this invention are water soluble or miscible. Generally, short chain alcohols or ketones are employed. The water-miscible solvents can be a combination of liquids. Specific examples of water-miscible solvents that are employed in this invention are acetone, methyl ethyl ketone, methyl alcohol, ethyl alcohol, propyl alcohol, and the like. Preferably, methyl alcohol or acetone are employed. Further, a mixture of these water-miscible solvents and an aromatic solvent such as xylene or toluene can be employed. Generally, the ratio of water-miscible solvent to aromatic solvent ranges from 3:1 to 1:3 by weight. Preferably, this ratio is 1 to 1 by weight.

The water-immiscible liquid contents of the capsule are capable of dissolving the mark-forming chromogenic compounds, if present. The water-immiscible liquid is volatile or non-volatile and can be comprised of one or more components. Examples are toluene, petroleum distillate, perchloroethylene, xylene, petroleum fractions and chlorinated diphenyls.

The chromogenic compounds (colorless dye materials) and polymeric mark-forming components that are employed in this invention vary widely. Examples of such mark-forming components are described on pages 5 to 9 of the previously mentioned U.S. Pat. No. 3,672,935, issued June 27, 1972.

Two preferred colorless reactants are (1) Crystal Violet Lactone, which is named 3,3-bis(4-dimethylaminophenyl)-6-dimethylaminophthalide and (2) benzoyl leuco methylene blue, which is named 3,7-bis(dimethylamino)-10-benzoyl phenothiazine. Other colorless dye materials which can be employed in this invention are:

a. 2'-anilino-6'-diethylamino-3'-methylfluoran;
b. 2'-methyl-6'-cyclohexylaminofluoran;
c. 3,3-bis(1-ethyl-2-methyl-indol-3-yl)phthalide;
d. 9-diethylaminospiro[1,2-H-benzo-(a)-xanthene-1,2,1'-phthalide];
e. 2'-chloro-6'-diethylamino-3'-methylfluoran; or
f. 3,3-bis(1-benzyl)-2-methyl-indol-3-yl)phthalide.

Preferred acidic polymeric materials useful in this invention include phenol polymers, phenol acetylene polymers, maleic acid-rosin resins, partially or wholly hydrolyzed styrene-maleic anhydride copolymers and ethylene-maleic anhydride copolymers, carboxy polymethylene and wholly or partially hydrolyzed vinyl methyl ether maleic anhydride copolymer and mixtures thereof.

Other representative acidic coating materials are oil-insoluble minerals or inorganic particulate solid material, represented by kaolin, attapulgite, silica gel, zeolites, and the like.

Kaolin is generally known and used in the papermaking industry as "china clay" and is outstandingly preferable as a particulate oil-insoluble and water-insoluble mineral material of acid characteristics necessary to color benzoyl leuco methylene blue, one of the chromogenic components, where that component is necessary. A white kaolin is used, and, because of its whiteness, its plate-like particle form, which gives it unparalleled coating properties in aqueous slurries, its universal abundance in supply, its historical general usage in the paper-making and paper-converting industries, and its low cost, it is an ideal material. Other types of particulate and substantially colorless water-and oil-insoluble minerals of the necessary acid properties are deemed equivalents of kaolin, some being bentonites.

Attapulgite can be used in this invention as an efficient colorless mineral reactant material to color those colorless chromogenic compounds of the novel ink of this invention that react on contact in an electron-donor-acceptor reaction, and, by reason of its high oil absorbency, is doubly useful as an absorbent reaction coating on paper to form color with such chromogenic compounds dissolved in oil as can be applied to it.

The material or materials chosen as the wall material of the microcapsules is inert with respect to the contents of the capsule and the other mark-forming components so that the wall material remains intact under normal storage conditions. Examples of wall material are gelatin alone or in combination with gum arabic, and many other hydrophilic colloid materials which are thoroughly described in the aforementioned patents and patent application.

In the process for removing the water-immiscible liquid contents of the gelatin-walled capsules without rupturing the capsule wall, the water-miscible solvent is maintained in physical isolation until such time as it is released. This is accomplished by several known techniques. Dipping, brushing, wiping, spraying and the like can be employed. A preferred method for applying the solvent is by employing a felt-tip marker.

The record member, if employed, consists of a base sheet or web member either of fibrous construction, such as paper, or of continuous structure, such as films of organic polymeric material.

The mark-forming components can be applied to the support sheet material by various methods known in the art, as are the respective amounts of each material and other materials employed to supplement these reactants. For example, see Columns 7 and 8 of U. S. Pat. No. 3,540,914.

When the mark-forming components are employed, the microcapsules' water-immiscible liquid contents contain a small amount of colorless dye material. The amount of colorless dye material generally ranges from 0.5 to 5.0 weight percent, preferably 1.0 to 2.5 weight percent.

The microcapsules are present in the support material either disposed therethroughout or as a coating thereon, or both. The capsules can be applied to the sheet material while still dispersed in the liquid vehicle in which they were manufactured which is followed by coating with the polymeric component. If desired, the capsules can be separated from the liquid vehicle and dispersed in a solution of the polymeric component to form a coating composition which can be applied to the sheet material. When either composition is disposed as a film on the support material and dried, the capsules are held therein subject to replacement of the liquid contained.

In another embodiment, just the microcapsules can be coated onto the sheet material. With such a sheet, a mixture of water-miscible solvent and polymeric material is employed.

As previously stated, the acidic polymeric material employed in this invention is located in the water-miscible solvent, in the capsule or on or within the sheet support material. The water-miscible solvent is present in such form that it is maintained isolated from the colorless dye material until it is desired to bring the mark-forming components into reactive contact to produce a distinctive mark. The colorless dye material or chromogenic compound is located in the capsule. The capsules are present in the support material either disposed therethroughout or as a coating thereon, or both.

By employing various combinations of support sheets and solvent applications, distinctive marks can be achieved. In one embodiment, the capsules and acidic material can be coated onto support material so as to form a substantially colorless decorative design. Application of the water-miscible solvent by means such as brushing or spraying then will produce a distinctive mark on the support material by bringing the colorless dye material and acidic color-activating material into reactive contact. Such contact will occur without rupture of the capsule wall due to the exchange between the original oily contents of the capsules and the solvent through the capsule walls.

In the instance where the mark-forming components are interspersed throughout a support sheet, the water-miscible solvent can be applied by a felt-tip marker to bring the mark-forming components into reactive contact. In this application, the form of the distinctive marking is left to the imagination of the individual applying the solvent with the felt-tip marker. Again, the distinctive mark is produced without rupture of the capsule wall due to the exchange of the original oil contents of the capsules and the solvent through the capsule walls.

By employing the first embodiment described above, a child for example, could produce a decorative design by merely scribbling on the coated support material with a felt-tip marker or brush containing the water-miscible solvent. In the second embodiment, a more advanced individual could write by employing the felt-tip marker as a stylus or such an individual could use the felt-tip marker to create a decorative design of his own choice.

Still another embodiment would be to coat various portions of the support material with capsules containing a wide variety of colorless, but colorable dyes. For example, the support material can be coated so that the application of the water-miscible solvent will produce blocks of different colors.

In all such variations, the capsules contain a mixture of water-immiscible liquid and colorless dye material. The polymeric material generally is present on the sheet or admixed with the water-miscible solvent. By diffusion of the water-miscible solvent through the capsule wall, the water-immiscible liquid contents are replaced. When mark-forming components are present and brought into contact by replacement of the capsule contents, a color reaction is produced without rupturing the capsule wall.

The advantages of this invention are further illustrated by the following example. The reactants and the proportions and other specific conditions are presented as being typical and should not be construed to limit the invention unduly.

EXAMPLE

Two homogeneous solutions were prepared. Less than 2 weight percent of Crystal Violet Lactone (CVL) and less than 2 weight percent benzoyl leuco methylene blue (BLMB) each were dissolved in an oil comprising a two-to-one mixture of chlorinated biphenyl and saturated hydrocarbon by weight. Each solution results in a blue color on sensitized record material.

Each solution was then encapsulated and coated onto paper by methods similar to those methods described in the aforementioned patents and patent application. In particular, the methods employed are those described in U.S. Pat. No. 3,672,935.

Paraphenylphenol resin, e.g., Durez 26141 or 26798, were admixed in a solvent of methyl alcohol or acetone. The resin-solvent mixtures were then applied to the coated paper with conventional felt-tip markers

without rupturing the capsules. Decorative blue marks appeared on all applications.

Although this invention has been described in considerable detail, it must be understood that such detail is for the purpose of illustration only and that many variations and modifications can be made by one skilled in the art without departing from the scope and spirit thereof.

What is claimed is:

1. A process for removing the water-immiscible liquid contents of capsules containing a mixture of an organic oil and at least one colorless but colorable chromogenic compound, the capsules being coated on a web or sheet as a finely dispersed phase, the capsules having walls at least partially consisting of hydrophilic colloid material, without rupturing the capsule walls, comprising the step of contacting the capsules on said web or sheet with water-miscible solvent selected from the group consisting of acetone, methyl ethyl ketone, methyl alcohol, ethyl alcohol, and propyl alcohol, thereby replacing the original liquid contents of said capsules with the water-miscible solvent by diffusion through the capsule walls continuing to a diffusion equilibrium state over a period of time.

2. A process according to claim **1** wherein the water-miscible solvent is admixed with an aromatic solvent wherein the ratio of water-miscible solvent to aromatic solvent ranges from 3:1 to 1:3 by weight.

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